NASA TT F-10,007

ROTATIONAL RELAXATION OF DIATOMIC MOLECULES

Ye.Ye.Nikitin

N66-21689

(ACCESSION NUMBER)	(THRU)
9 (PAGES)	1 (CODE)
(NASA CR OR TMX OR AD NUMBER)	34 (CATEGORY)

FACILITY FORM 602

Translation of "Vrashchatel'naya relaksatsiya dvukhatomnykh molekul". Doklady Akademii Nauk SSSR, Fizicheskaya Khimiya, Vol.161, No.3, pp.637-640, 1965.

GPO PRICE $ _____

CFSTI PRICE(S) $ _____

Hard copy (HC) 1.00

Microfiche (MF) .50

ff 653 July 65

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON FEBRUARY 1966

E

ROTATIONAL RELAXATION OF DIATOMIC MOLECULES

**/637

Ye.Ye.Nikitin*

21689

Relaxation equations for the rotational distribution function of diatomic molecules, colliding with an atom or electron under the conditions $\omega_j \tau \lesssim 1$ (ω_j = angular frequency; τ = = collision time), are derived. A typical application to the rotational relaxation of molecules, in a thermal reservoir of light particles and taking the conservation of the Boltzmann distribution into consideration, is given for the case of inelastic excitation of molecular rotation in N_2, H_2, and I_2 in an atmosphere of helium.

The calculation of the rate of energy exchange between the rotational and translational degrees of freedom in a nonequilibrium gas is of interest for a number of problems in kinetics (Bibl.1). Successive theoretical calculation of the cross sections for rotational excitation meets the difficulty that the various versions of the perturbation theory are usually inapplicable on account of the strong interaction responsible for the rotational transitions. The only exception is the case of adiabatic collisions, when the angular frequency ω_j is substantially greater than the reciprocal collision time $1/\tau$ [rotational transitions in hydrogen at relatively low temperatures (Bibl.2)].

In this paper we present a derivation of the relaxation equations for the rotational distribution function of diatomic molecules colliding with a

---

* Presented by Academician V.N.Kondrat'yev, Sept.2, 1964.

** Numbers in the margin indicate pagination in the original foreign text.

particle C (atom or electron) under the condition $\omega_j \tau \lesssim 1$. Setting $\omega_j \sim$ $\sim (B/\beta)^{1/2}$, $\tau \sim (\mu\beta)^{1/2}/\alpha$, where $B = \hbar^2/Mr_e^2$ is the rotational constant of the molecule, $\beta = 1/kT$, μ is the reduced mass of AB and C, and $1/\alpha$ is the radius of action of the potential (all parameters of the dimension of energy are expressed in frequency units), we find $\bar{\omega}\tau \sim \mu^{1/2}/M^{1/2}\alpha r_e$. Thus, the condition $\bar{\omega}\tau \lesssim 1$ is satisfied either when the radius of action of the potential is significantly smaller than the equilibrium interatomic distance AB, or when the ratio of the masses μ/M is small.

Bernstein, Dolgarno, Massey and Percival (Bibl.3) have recently proposed a statistical theory for estimating the strong coupling between the rotational states of the molecule on collision, based on an idea similar to random phase approximation in calculating the elastic scattering cross section. The elements of the scattering matrix $S(j, l; j', l')$ from the channel j, l (j being the moment of the molecule and l the moment of relative motion) to the channel j', l' are assumed to be equal at modulo in mean (after averaging over a small energy interval), provided that l and l' do not exceed a certain value l_0. The quantity l_0 is defined from the condition that the total probability of transition from the channel j, l_0, calculated by the distorted wave approximation method, shall be of the order of unity. Thus, the condition $|j' - j| \leq 2l_0$ is obtained for the variation of the moments. Assuming the rotation to be quasi-classical ($j, j' \gg 1$), let us consider the cases corresponding to various ratios of the quantities j, j', and l_0.

1. The moment of relative motion l_0 is significantly greater than the moments $\bar{j}$, $\bar{j}'$ making the principal contribution to the mean rotational energy ($1 \ll \bar{j}, \bar{j}' \ll l_0$). We note first of all that the static character of the distribution by levels j' means the equiprobable distribution by rotational energies;

this follows from the coincidence of the phase volume $(2j + 1)dj$ with $d\varepsilon$, at accuracy to within a constant. Then the partial velocities of transition between the states $\varepsilon \to \varepsilon'$ of the diatomic molecule in the thermal reservoir may be found on the basis of the following considerations: De-activation at any level is equiprobable (condition $j' \ll l_0$), the probability of activation is determined by the probability of de-activation according to the principle of /638 quasi-static equilibrium, while the total cross section for inelastic collision is $\pi l_0^2/k^2$ ($k = \mu v/\hbar$) (Bibl.3). An integral equation for the distribution function $x(\varepsilon)$, corresponding to a probability of this type, has been discussed by Hoare (Bibl.4). For the case we are considering, this equation will have the form

$$\frac{dx(\varepsilon)}{dt} = Z_1 \int [K(\varepsilon' \to \varepsilon)\, x(\varepsilon')\, d\varepsilon' - K(\varepsilon \to \varepsilon')\, x(\varepsilon)\, d\varepsilon'],$$
$$K(\varepsilon' \to \varepsilon) = \beta \exp(\beta\varepsilon') \int_{\max(\varepsilon,\, \varepsilon')}^{\infty} \frac{1}{s} \exp(-\beta s)\, ds, \tag{1}$$

where $Z_1 = \left\langle v\pi \frac{l_0^2}{k^2} \right\rangle n_c$.

Multiplying eq.(1) by ε and integrating, we find the following equation for the relaxation of the mean rotational energy $\bar{\varepsilon}$:

$$\frac{d\bar{\varepsilon}}{dt} = -k_1(\bar{\varepsilon} - kT), \quad k_1 = \frac{1}{2} Z_1. \tag{2}$$

Thus, the relaxation of $\bar{\varepsilon}$ proceeds according to a simple exponential law. Equation (2) relates the experimentally observed time of partial relaxation τ_1 (observed, for instance, from the thickness of the shock-wave front) with the quantity l_0 characterizing the anisotropy of the intermolecular potential. Here l_0 is not directly related to the probability of a one-quantum rotational transition [in this connection, see the footnote on page 303 of the book by Kondrat'yev (Bibl.1)]. Putting $l_0 = \mu v R_0/\hbar$, we find $\tau_1 = 2/\pi R_0^2 \bar{v}$, with the condition $j \ll l_0$ imposing an upward restriction on R_0:

$$\sqrt{\frac{M}{\mu}}\, r_e \ll R_0. \qquad (3)$$

2. The moment of relative motion l_0 is substantially smaller than $\bar{j}$ and $\bar{j}'$ ($\bar{j}, \bar{j}' \gg l_0 \gg 1$). The relaxation may be described by levels where the distribution function obeys the Fokker-Planck equation [cf., e.g., (Bibl.5)]

$$\frac{\partial x(\varepsilon)}{\partial t} = \frac{1}{2}\frac{\partial}{\partial \varepsilon}\left[Z_2 \langle \Delta\varepsilon^2 \rangle \beta \left(1 + \frac{\partial}{\beta\, \partial \varepsilon}\right)\right] x(\varepsilon). \qquad (4)$$

The factor $Z_2 \langle \Delta\varepsilon^2 \rangle$ equals the mean-square energy imparted to the molecule in unit time. Determining the number of collisions Z_2 as $v\pi R_0^2 n_e$, the quantity $\langle \Delta\varepsilon^2 \rangle$ may be calculated from the Π-distribution function of energy transfer, whose limits are defined respectively by the relation $\Delta j_{max} = 2l_0$ or $\Delta\varepsilon^{\pm} = \pm 4\sqrt{Bl_0}\sqrt{\varepsilon}$. In this way, we obtain

$$^1/_2 Z_2 \langle \Delta\varepsilon^2 \rangle = \langle v\pi R_0^2\, {}^8/_3 B l_0^2 \rangle n_e \varepsilon, \qquad (5)$$

where the averaging on the right-hand side has been performed over the equilibrium velocity distribution function. The solution of eq.(4) is well known for the case where the mean-square transferred energy is proportional to the energy (Bibl.5, 6).

The distinctive feature of a relaxation system is that, first, the mean energy (first moment of the distribution function) relaxes independently of the higher moments, in analogy to eq.(2), and the corresponding velocity constant k_2 is equal to $\beta Z_2 \langle \Delta\varepsilon^2 \rangle / \varepsilon$. Assuming, for simplicity, that R_0 does not depend on v, we find

$$k_2 = \frac{1}{\tau_2} = \bar{v}\pi R_0^2 \frac{16}{3} \frac{R_0^2}{r_e^2} \frac{\mu}{M}. \qquad (6)$$

Second, the initial Boltzmann distribution relaxes to the final distribution through a sequence of distributions of the same type. Although the form of the relaxation equations for $\bar{\varepsilon}$ obtained from eqs.(1) and (6) is the same,

the latter conclusion is nevertheless untrue for the distribution function /639 of eq.(1). The condition of quasi-classicity of the collision and the condition $j \gg l_0$ takes the form

$$\lambda \ll R_0 \ll r_e \sqrt{\frac{M}{\mu}}, \tag{7}$$

where λ is the length of the wave of relative motion of AB and C.

3. The moment of relative motion l_0 is substantially less than j', and the relative motion of AB and C is not quasi-classical ($\bar{j}, \bar{j}' \gg l_0 \sim 1$). Such a situation corresponds to the collision of a slow electron with a diatomic molecule, l_0 in this case denoting the maximum effective moment contributing to the scattering. Under typical conditions, the interaction is weak and the cross section can be calculated in Born's approximation. For quasi-classical rotation of the molecule and far from the threshold the cross section is (Bibl.7):

$$\sigma(j', j) = \sum_m N_m \frac{2j'+1}{(2m+1)^2} C^2(j, j', m\,(000)),$$
$$N_m = \int d\omega \left| \int_0^\infty r^2 \frac{2\mu}{\hbar^2} V_m(r) J_m(\Delta k r)\, dr \right|^2, \tag{8}$$

where the $V_m(r)$ are the coefficients of the expansion of the electron-molecule potential into Legendre polynomials $P_m(\cos\theta)$ and N_m does not depend on j under the condition that $\hbar^2(k^2 - k'^2)/\mu \gg Bjl_0$. Then, $Z_3\langle\Delta\varepsilon^2\rangle$ may be calculated in the closed form:

$$\tfrac{1}{2} Z_3 \langle \Delta\varepsilon^2 \rangle = \left[B \sum_m \langle v N_m(v) \rangle P_m'(1)/(2m+1) \right] \varepsilon. \tag{9}$$

Thus in the case 3, the kinetics of relaxation is analogous to the kinetics of relaxation for the case 2, and the velocity constant of relaxation of mean energy will be

$$k_3 = \beta B \sum_m \langle v N_m \rangle \frac{P_m'(1)}{2m+1}. \tag{10}$$

The condition of applicability of the first approximation of the perturba-

tion theory to slow electrons may be formally expressed by the collision radius $R_0 \sim \sqrt{\sigma}$ in the form of

$$R_0 \lesssim \lambda. \tag{11}$$

The three limiting cases of eqs.(3), (7), and (11) permit a qualitative tracing of the effect of the variation in the reduced mass on the velocity of rotational relaxation. As the ratio μ/M decreases, the velocity of relaxation also decreases. The relative contribution of the inelastic processes to the velocity of relaxation of energy of the light participants, however, will increase (relative to the elastic processes) by a factor of $16\ R_0^2/3r_e^2$ in the case of the condition (7), and by a factor of $\sim \frac{M}{\mu}\ \frac{B}{kT}$ in the case of condition (11). Conditions under which these factors are of the respective orders of 10 and 100 are highly probable.

Let us now discuss one specific application of eqs.(4) and (10). According to these expressions, the rotational relaxation of molecules in a thermal reservoir of light particles (electrons) may be described by an equation taking account of the conservation of the Boltzmann distribution:

$$\frac{dT_{rot}}{dt} = -k_3(T_{el})[T_{rot} - T_{el}], \tag{12}$$

where T_{rot} is the rotational temperature of the molecular gas and T_{el} the /640 temperature of the electrons. Let us assume a system of rotating molecules and electrons to be isolated, with the Maxwellian distribution of the electrons maintained by reciprocal collisions. Obviously, the relaxation equation for the electron temperature should then be of the form

$$\frac{dT_{el}}{dt} = -k_3(T_{el})[T_{el} - T_{rot}]. \tag{13}$$

This equation is nonlinear; it will, in particular, be valid even in the case where T_{rot} = const. Then eq.(13) will describe the variation of the

electron temperature in the process most effective for slow electrons: inelastic excitation of molecular rotation. In linear approximation, $k_3(T_{el})$ should be replaced by $k_3(T_{rot})$. The limits of applicability of the linear approximation are readily found, since the temperature dependence of k_3 is known in principle. Thus, for quadrupole-monopole interaction, which is most effective for homonuclear molecules, k_3 will be equal to

$$k_3 = {}^{16}/_{15}\bar{v}\pi a_0^2 q^2 B\beta \sim T^{-1/2}, \tag{14}$$

where q is the quadrupole moment of A_2 (in a.u.). A comparison of eq.(14) with the results of direct numerical calculations of k_3' (Bibl.7) as the limit of the ratio

$$k_3' = \lim_{T_{el}\to T} (dT_{el}/dt)/(T - T_{el}) \tag{15}$$

for the case of N_2 indicates agreement between them. A discrepancy of about 10% is obtained only in the low-temperature region (T = 100°K), owing to the insufficient accuracy of the quasi-classic approximation (for this case, $\bar{j} \sim 6$). Hence we find, for example, that the linear relaxation equation for T_{rot} = = 300°K and T_{el} = 700°K exaggerates the velocity of the initial stage of relaxation by a factor of $\sqrt{7/3} \sim 1.5$, which is in agreement with the numerical results obtained by Dolgarno (Bibl.7).

In atomic-molecular collisions, eq.(4) is applicable to the description of the rotational relaxation of molecules of the type of I_2 in an atmosphere of light gas (He), under the conditions, for instance, of photoexcitation [cf. page 305 (Bibl.1)]. As for eqs.(1) and (2), they yield a reasonable estimate for R_0 when applied to the experimental data on the rotational relaxation of hydrogen and nitrogen: the value of R_0 is smaller by a factor of 2 to 3 than the van der Waals radius of the colliding molecules.

BIBLIOGRAPHY

1. Kondrat'yev, V.N.: Kinetics of Chemical Reactions in Gases (Kinetika khimicheskikh gazovykh reaktsiy). Izd. Akad. Nauk SSSR, 1958.

2. Takayanagi, K.: Suppl. Progr. Theor. Phys., Vol.25, p.1, 1963.

3. Bernstein, R.B., Dolgarno, A., Massey, H., and Percival, I.C.: Proc. Roy. Soc., Vol.A274, p.427, 1963.

4. Hoare, M.R.: Mol. Phys., Vol.4, p.465, 1961.

5. Nikitin, Ye.Ye.: The Modern Theories of Thermal Dissociation and Isomerization of Molecules in the Gas Phase (Sovremennyye teorii termicheskogo raspada i izomerizatsii molekul v gazovoy faze). Nauka, 1964.

6. Losev, S.A. and Osipov, A.I.: Usp. Fiz. Nauk, Vol.74, p.394, 1961.

7. Dolgarno, C.A. and Moffett, R.J.: Acad. Sci. India, Vol.A33, p.511, 1963.

Institute of Chemical Physics
USSR Academy of Sciences

Received
September 1, 1964